Characterization of Construction Materials
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Lecture 20
X Ray Diffraction Qualitative Phase Analysis Part 2

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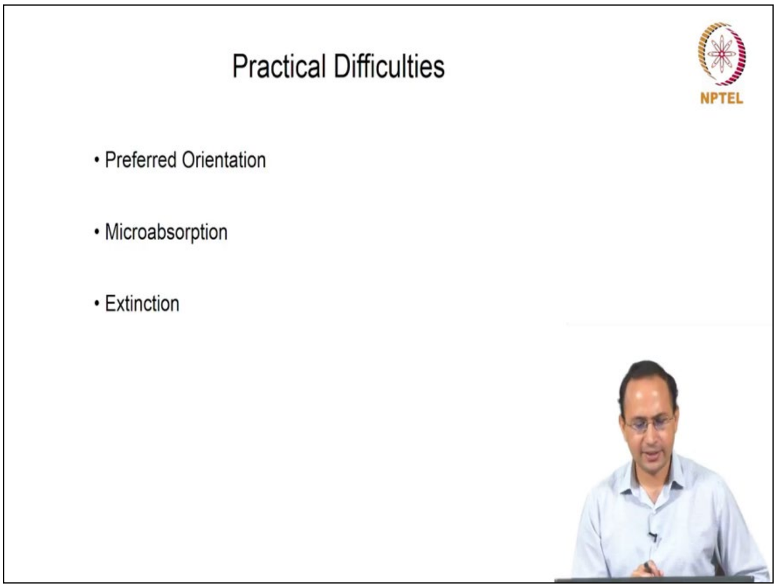

Practical Difficulties

- Preferred Orientation
- Microabsorption
- Extinction

Let us come to some practical difficulties, now. We often encounter these issues like, preferred orientation, microabsorption, extinction. We will learn about it.

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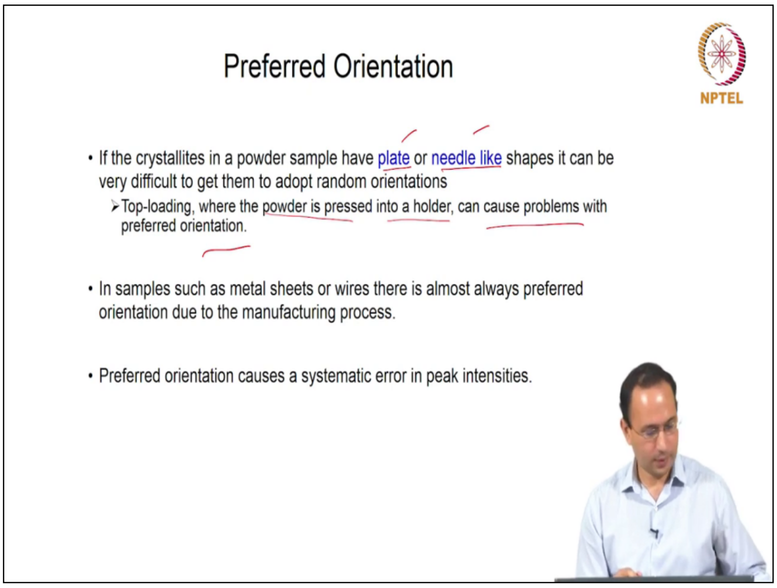

Preferred Orientation

- If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt random orientations
  - Top-loading, where the powder is pressed into a holder, can cause problems with preferred orientation.
- In samples such as metal sheets or wires there is almost always preferred orientation due to the manufacturing process.
- Preferred orientation causes a systematic error in peak intensities.

So what is 'preferred orientation'? Suppose you have a phase, which is in the shape of plates, for an example, having a plate like structure, what will happen? The plates will most likely tend to stack. It will tend to stack in particular direction, because it will depend on what kind of plates we have, and what the aspect ratio is. But if the crystallites in the powder sample have plate or needle like shapes, you can guess that it will be very hard to get them to adopt random orientations because they are likely to orient in particular direction just because of geometry.

Can you think about this? Suppose, you have plate-like structure, it will tend to stack, what does that imply? If you have preferred orientation, your intensities will be stronger.

That means, the intensity you calculate will be quite different because you have a strong preferred orientation, just because of the phase geometry. Usually when you have plates or needle like shapes, you often encounter this. We will come back to the sample preparation in the next lecture. There are different ways to prepare samples – Top-loading, where the powder is pressed into a holder, can cause problems with preferred orientation.

We will see how to avoid that. But, simple thing to remember is, when you have these kinds of geometries you have to think about whether you are getting preferred orientation or not? Or how can you avoid it?

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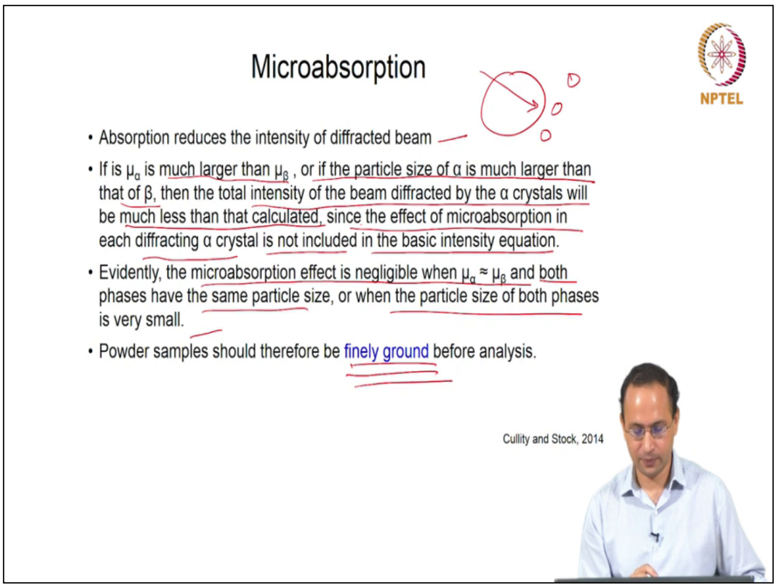

Microabsorption

- Absorption reduces the intensity of diffracted beam
- If is μ_α is much larger than μ_β , or if the particle size of α is much larger than that of β, then the total intensity of the beam diffracted by the α crystals will be much less than that calculated, since the effect of microabsorption in each diffracting α crystal is not included in the basic intensity equation.
- Evidently, the microabsorption effect is negligible when $\mu_\alpha \approx \mu_\beta$ and both phases have the same particle size, or when the particle size of both phases is very small.
- Powder samples should therefore be finely ground before analysis.

Cullity and Stock, 2014

Another thing is Microabsorption. You know about absorption. Absorption reduces the intensity of diffracted beam. Now, if you have two phases, alpha and beta, and if mu alpha is much larger than mu beta. Now, we are talking about absorption coefficient, if mu alpha is much greater than mu beta or if the particle size of alpha is much larger than beta, then total intensity of beam diffracted by alpha crystals will be much less than calculated, because its absorption coefficient is quite high, in one case, when mu alpha is greater than mu beta, and if the particle size is bigger, then it will take time for the diffracted beam to pass through. So, there will be lot of absorption. That will affect the intensity. That is the idea.

Since the effect of microabsorption in each diffracting alpha crystal is not included in the basic intensity equation. We have not considered that in our basic intensity equation. What is the absorption happening within your alpha crystals. So, we can see that when mu alpha is equal to mu beta, for example and both the phases have the same particle size, then you do not see this. The microabsorption effect is negligible.

So what we do? Normally in powder sample you have to grind the powder, to make it really fine. We will come back to sample preparation. But why do we grind samples? It is to avoid the microabsorption, which is one of the reasons. You have to make sure that you have very small sizes. If the size is big, then you will have microabsorption and the intensity will reduce.

So this is what you have to do before analysis; you have to make sure you have finely ground powder samples.

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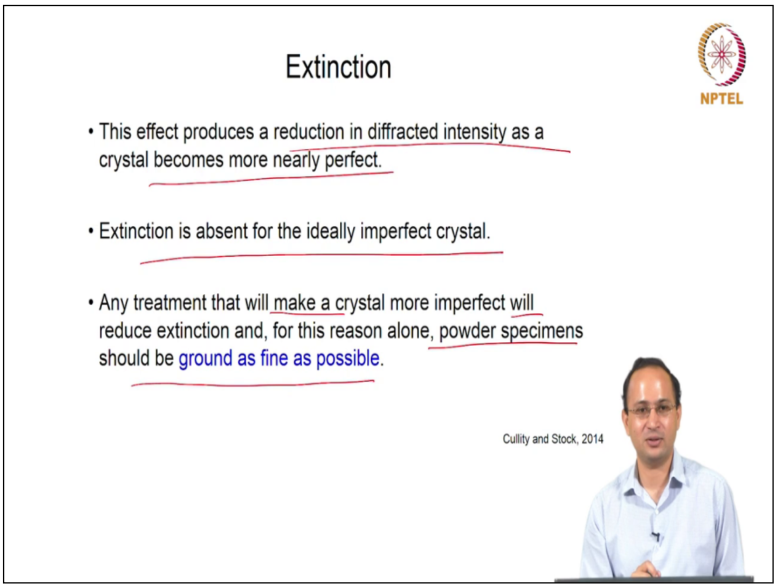

Extinction

- This effect produces a reduction in diffracted intensity as a crystal becomes more nearly perfect.
- Extinction is absent for the ideally imperfect crystal.
- Any treatment that will make a crystal more imperfect will reduce extinction and, for this reason alone, powder specimens should be ground as fine as possible.

Cullity and Stock, 2014

Another thing you have to think about is extinction. Extinction means disappearance. So, this effect produces reduction in the diffracted intensity as a crystal becomes more nearly perfect. Extinction is absent for the ideally imperfect crystals. You always have some important imperfections. So, any treatment which will make a crystal more imperfect will reduce extinction, because then you get secondary diffraction.

So, we are not going in detail, but the idea is, if you have a powder sample, it should be ground as fine as possible to reduce the extinction. In perfect crystals, you will find extinction and some peaks will be missing.

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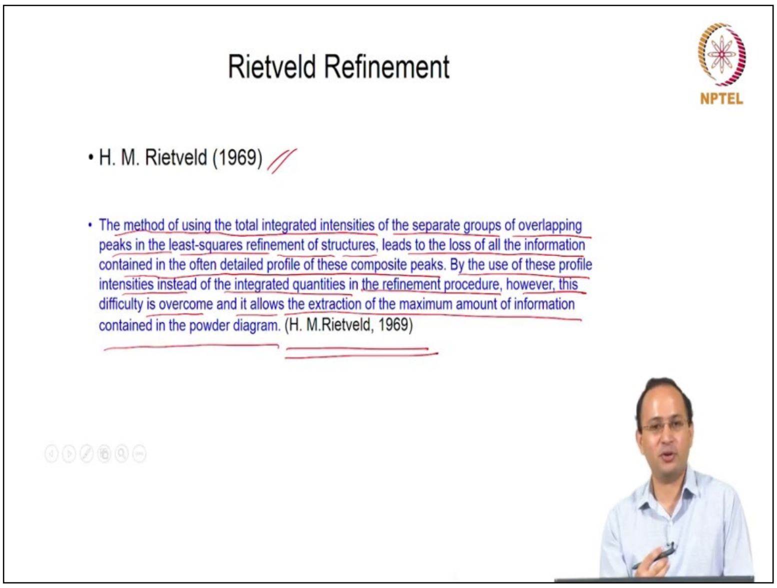

Rietveld Refinement

- H. M. Rietveld (1969)
- The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram. (H. M.Rietveld, 1969)

We have talked about couple of methods, like internal standard method, external standard method, but Rietveld refinement is a very commonly used method these days. It was proposed by Hugo Rietveld in 1969. It was a very important pioneering work in 1969. So, far we have been using individual peaks, integrated intensities, even though we are using integrated intensities, we are calculating area under the curve.

So, the method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to loss of all the information contained in the often detailed profile of these composite peaks. You have a detailed profile.

By the use of these profile intensities instead of the integrated quantities in the refinement process, however, this difficulty is overcome and it allows the extraction of maximum amount of information contained in the powder diagram.

So we have a powder diffractogram, diffraction pattern where you have multiple peaks. Why not use the whole pattern? That is the idea, rather than looking at individual peaks. A lot of issues with that, might be overlap there are a lot of factors which can play role in affecting the intensity, if you are looking at one or two peaks right. So idea is looking at the whole pattern.

Now, you can appreciate what is the importance of this Rietveld. We are looking at the whole pattern rather than looking at individual peaks.

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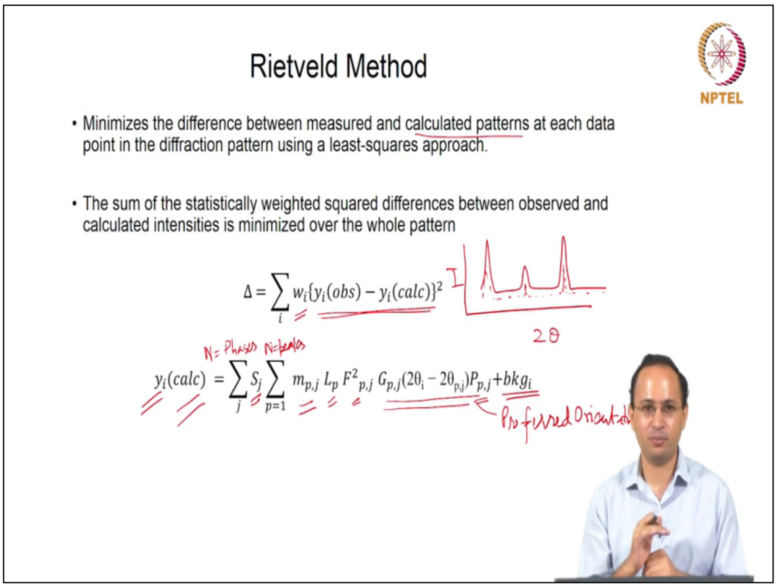

Rietveld Method

- Minimizes the difference between measured and calculated patterns at each data point in the diffraction pattern using a least-squares approach.
- The sum of the statistically weighted squared differences between observed and calculated intensities is minimized over the whole pattern

$$\Delta = \sum_i w_i\{y_i(obs) - y_i(calc)\}^2$$

$$y_i(calc) = \sum_j S_j \sum_{p=1} m_{p,j}\, L_p\, F^2{}_{p,j}\, G_{p,j}(2\theta_i - 2\theta_{p,j}) P_{p,j} + bkg_i$$

So what is it? What is the Rietveld method, it minimizes the difference between measured and calculated patterns at each data point in the diffraction pattern using a least-squares approach. You have a diffraction pattern, simplified diffraction pattern (Refer drawing in slide). This is the measured diffraction.

Now, we calculate diffraction pattern. How do we calculate? First of all you have to know, what the phases in your sample are. Qualitative phase analysis you have to carry out. We can then calculate what the intensity will be. So you refine, you basically calculate the pattern.

It is put as dot dot dot (Refer drawing in slide). What you are doing is you are minimising this difference. So, the sum of the statistically weighted square differences, w_i is the weighted average and we see that, we are minimizing the square of observed intensity minus calculated intensity. That is the function and we are trying to minimize it.

$$\Delta = \sum_i w_i\{y_i(obs) - y_i(calc)\}^2$$

So, structure refinement is an essential part of practical crystallography and must be distinguished from structure solution, it is the refinement not the solution. Refinement, as the name suggests, implies taking an approximate model of the structure and refining it so that the diffraction data calculated from the model structure has a closer resemblance to the observed data.

It cannot be emphasized strongly enough that it is the model structure that is refined, not the data; we are not refining the data, we are refining the model structure. So, how do we do it? See the second equation. So, you understand what we are minimizing. We are minimizing the weighted square difference between observed and calculated intensity.

$$y_i(calc) = \sum_{j}^{N1=phases} S_j \sum_{p=1}^{N2=peaks} m_{p,j} L_p F_{p,j}^2 G_{p,j}\left(2\theta_i - 2\theta_{p,j}\right) P_{p,j} + bkg_i$$

Observed intensity is what you get from your experiments and calculated intensity is what we have to calculate. So, how can we express calculated intensity? See, all these terms should be most of the terms, should be familiar to you. ‘m’ is multiplicity factor. So, we are looking at, here are number of phases and this is number of peaks. See, now we have multiple phases and each phase will give you multiple peaks.

So, to get the whole pattern you have to summate over all the peaks of one phase and then sum that over all the phases. So, for each phase, just look at this term first, this is for each phase you already know, multiplicity factor, Lorentz-polarization factor, structure factor, what this one? This is shape function. We will come back to it, as to why it appears here, because we are predicting, what kind of shape, it is going to take.

Diffraction, you know that will have some peak shape. So, you have to simulate that shape. So, this is that shape function. ‘P’ is preferred orientation correction, if needed. In some cases you may need it. Preferred orientation correction; and then the background (bkg), you always have some background. So, you know the background then you are adding this.

Now that you have done it for one phase, you have to summate over (S_j). So, this is a scaling factor, you have to scale it. Summate over ‘N’ phases. So, this is your calculated intensity (y_i(calc)). So, idea is again we are trying to simulate the profile, then compare it with the observed profile, then minimize the error.

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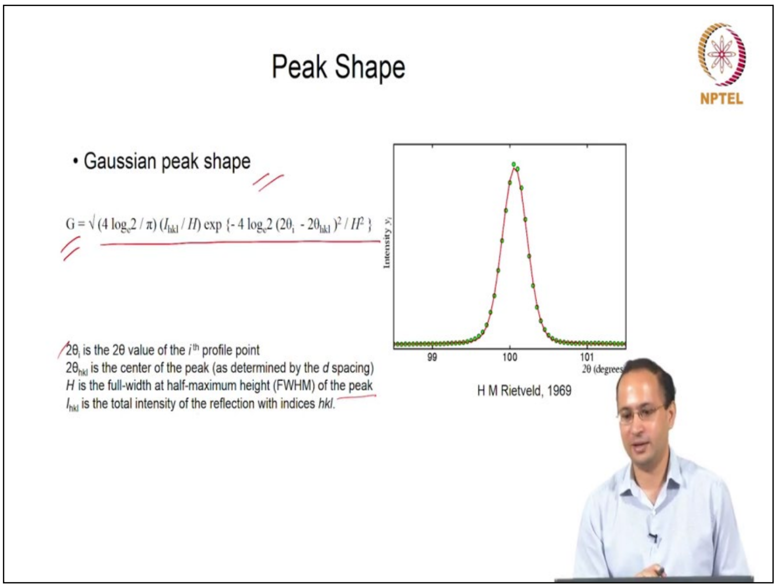

Peak Shape

- Gaussian peak shape

G = √ (4 log$_e$2 / π) (I_{hkl} / H) exp {- 4 log$_e$2 (2θ$_i$ - 2θ$_{hkl}$)^2 / H^2 }

2θ$_i$ is the 2θ value of the *i* th profile point
2θ$_{hkl}$ is the center of the peak (as determined by the *d* spacing)
H is the full-width at half-maximum height (FWHM) of the peak
I_{hkl} is the total intensity of the reflection with indices *hkl*.

H M Rietveld, 1969

So, how do we model the peak shape? You can use different functions. So, this is a simple example, where you use Gaussian peak shape. So, we assume that the peak shape, wherever you are getting the diffraction, has this Gaussian distribution. So, this is the function here:

$$G = \sqrt{}\left(4\ln\frac{2}{\pi}\right)\left(\frac{I_{hkl}}{H}\right)\exp\left\{\frac{-4\ln 2\,(2\theta_i - 2\theta_{hkl})^2}{H^2}\right\}$$

So, you know all these here. 2θ$_i$ here is the 2θ value at the ith profile point. We are looking at now one point, we are trying to simulate. 2θ$_{hkl}$ is the center of the peak. H is the full width at half maximum (FWHM) of the peak and I$_{hkl}$ is the total intensity.

So it is similar to the Gaussian function. We are just trying to use that function to fit this peak. This is one of the functions you use, but may not work, so you have different functions.

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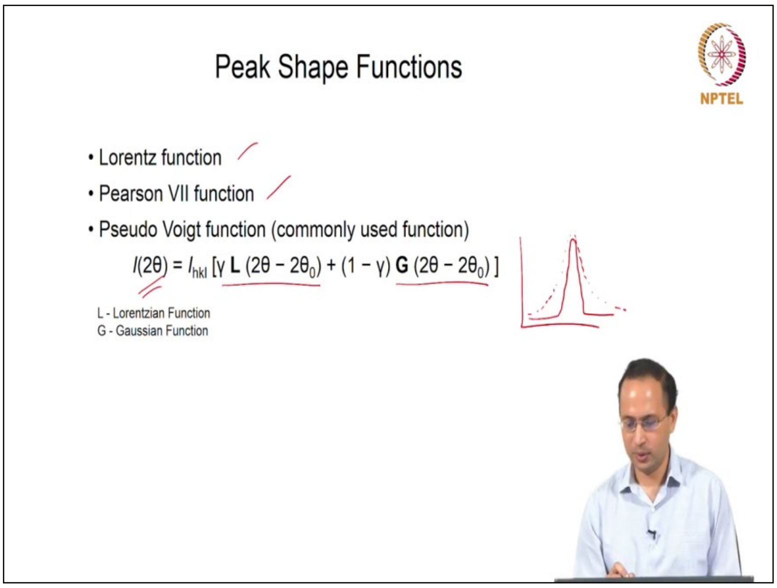

Peak Shape Functions

- Lorentz function
- Pearson VII function
- Pseudo Voigt function (commonly used function)

$I(2\theta) = I_{hkl}\,[\gamma\,\mathbf{L}\,(2\theta - 2\theta_0) + (1 - \gamma)\,\mathbf{G}\,(2\theta - 2\theta_0)]$

L - Lorentzian Function
G - Gaussian Function

You can use Lorentz function also. You can use Pearson VII function. Only difference between Lorentz and Pearson VII function is, Pearson's VII function is to the power 'm' of the Lorentz function. I am not going into detail, if you refer to any elementary mathematics textbook, you will be able to find these functions. But most commonly these days we are using a Pseudo Voigt function.

It is nothing but the combination of Gaussian and Lorentz function you see, it can be written as:

$$I(2\theta) = I_{hkl}[\gamma \boldsymbol{L}(2\theta - 2\theta_0) + (1-\gamma)\boldsymbol{G}(2\theta - 2\theta_0)]$$

L for Lorentzian function and G for Gaussian function. So, you are simply combining these two. Just to get the better peak shape. Basically if you look at the Gaussian will be something like this (solid line in graph, Figure 1) and Lorentzian will look something like this (dotted line in graph, Figure 1), that's the difference, but you can refer to any book. So, this is commonly used these days in Rietveld refinement.

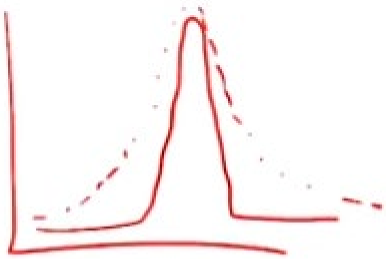

Figure 1 Gaussian and Lorentzian distribution

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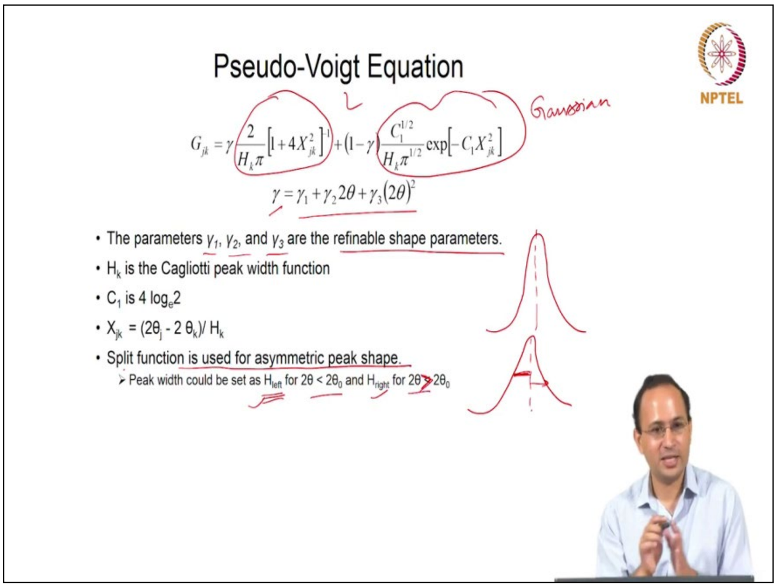

Pseudo-Voigt Equation

$$G_{jk} = \gamma \frac{2}{H_k \pi}\left[1+4X_{jk}^2\right]^{-1} + (1-\gamma)\frac{C_1^{1/2}}{H_k \pi^{1/2}}\exp\left[-C_1 X_{jk}^2\right]$$

$$\gamma = \gamma_1 + \gamma_2 2\theta + \gamma_3 (2\theta)^2$$

- The parameters γ_1, γ_2, and γ_3 are the refinable shape parameters.
- H_k is the Cagliotti peak width function
- C_1 is 4 $\log_e 2$
- $X_{jk} = (2\theta_j - 2\theta_k)/ H_k$
- Split function is used for asymmetric peak shape.
  - Peak width could be set as H_{left} for $2\theta < 2\theta_0$ and H_{right} for $2\theta > 2\theta_0$

So, coming back to Pseudo-Voigt, we said it is a combination of Gaussian function and Lorentzian function.

$$G_{jk} = \gamma \frac{2}{H_k \pi}\left[1+4X_{jk}^2\right]^{-1} + (1-\gamma)\frac{C_1^{1/2}}{H_k \pi^{1/2}}\exp\left[-C_1 X_{jk}^2\right]$$

So, $\frac{C_1^{1/2}}{H_k \pi^{1/2}}\exp\left[-C_1 X_{jk}^2\right]$ is the term for Gaussian, and $\left[1+4X_{jk}^2\right]^{-1}$ is the Lorentzian, we are taking fractions. So, you see here some parameters:

$$\gamma = \gamma_1 + \gamma_2 2\theta + \gamma_3 (2\theta)^2$$

In Rietveld refinement, you can refine these γ_1, γ_2, γ_3. They are the refineable shape parameters. By refining these, you can adjust the peak shape functions.

So, now you know how to simulate or model a peak. It could be a combination of Gaussian and Lorentzian in this case. Now, sometimes you may have asymmetry also, not all the time will you have a symmetric peak. So, how do we address that?

So, we can use the split function. Then, the peak width can be set. H is the full width half maximum. You can define H. Peak width could be set as H_{left} for $2\theta < 2\theta_0$ and H_{right} for $2\theta > 2\theta_0$. Whether you are in the left hand side or right hand side, you can define. So, this can be used when you have asymmetric peaks which you will be able to identify by looking at your diffraction pattern.

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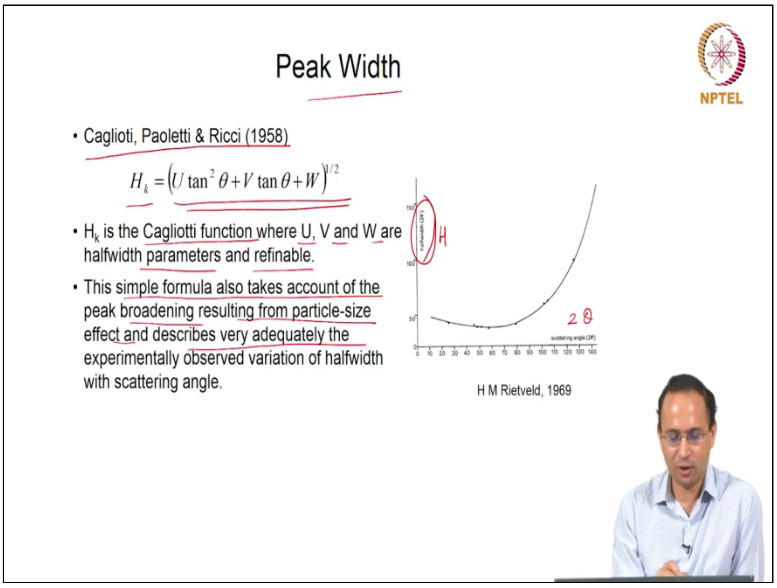

Peak Width

- Caglioti, Paoletti & Ricci (1958)

$$H_k = \left(U \tan^2 \theta + V \tan \theta + W\right)^{1/2}$$

- H_k is the Cagliotti function where U, V and W are halfwidth parameters and refinable.
- This simple formula also takes account of the peak broadening resulting from particle-size effect and describes very adequately the experimentally observed variation of halfwidth with scattering angle.

H M Rietveld, 1969

Now, we took care of the peak profile, it is also important to look at the peak width. So basically, we can use the Cagliotti function H_k

$$H_k = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$$

The Cagliotti function, H_k depends on θ. So, it will not be same at all angles and you cannot assume it will be uniform.

So, H_k is the Cagliotti function, where U,V, and W are the halfwidth parameters and are refinable. When you do quantitative analysis, you will see these U, V, and W. Where do they come from? Because your peak width depends on this. So, here is a plot (in figure in slide), where you see that halfwidth H, depends on the scattering angle, 2θ. You see that H is not constant; it is changing, depending on θ.

It depends on the expression $H_k = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$. So, it depends on θ. So, this simple formula also takes account of the peak broadening resulting from particle size effects and describes very adequately the experimentally observed variation of halfwidth with scattering angle.

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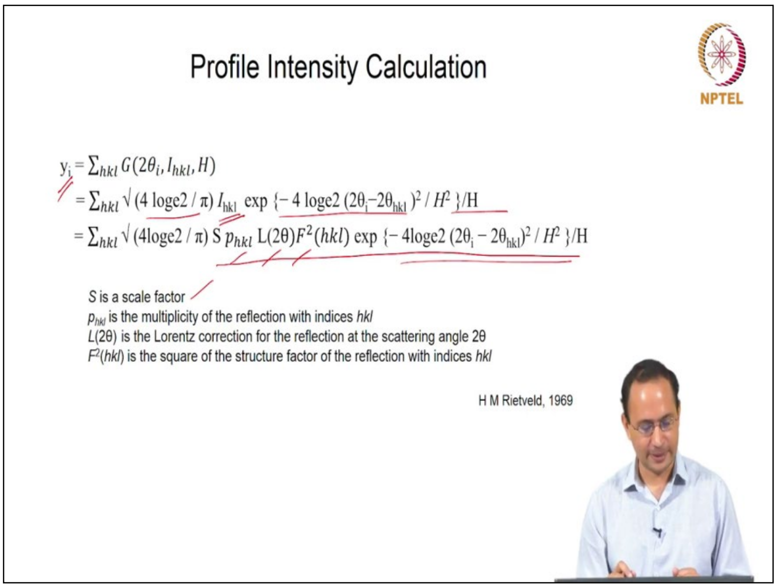

Profile Intensity Calculation

$y_i = \sum_{hkl} G(2\theta_i, I_{hkl}, H)$

$= \sum_{hkl} \sqrt{(4\,\mathrm{loge}2/\pi)}\, I_{hkl}\, \exp\{-4\,\mathrm{loge}2\,(2\theta_i - 2\theta_{hkl})^2/H^2\}/H$

$= \sum_{hkl} \sqrt{(4\mathrm{loge}2/\pi)}\, S\, p_{hkl}\, L(2\theta) F^2(hkl)\, \exp\{-4\mathrm{loge}2\,(2\theta_i - 2\theta_{hkl})^2/H^2\}/H$

S is a scale factor

p_{hkl} is the multiplicity of the reflection with indices *hkl*

$L(2\theta)$ is the Lorentz correction for the reflection at the scattering angle 2θ

$F^2(hkl)$ is the square of the structure factor of the reflection with indices *hkl*

H M Rietveld, 1969

So, now we have all the information and we know how to model the peaks. So, basically what we can write is y_i; we are calculating the intensity. We have measured intensity. Now idea is to calculate intensity, then minimize the difference. So, we already know this expression, and these are some constants based on the kind of function you have chosen.

$$y_i = \sum\nolimits_{hkl} G(2\theta_i, I_{hkl}, H)$$

$$= \sum\nolimits_{hkl} \sqrt{\left(4\ln\frac{2}{\pi}\right)}\,(I_{hkl})\,\exp\left\{\frac{-4\ln 2\,(2\theta_i - 2\theta_{hkl})^2}{H^2}\right\}/H$$

$$= \sum\nolimits_{hkl} \sqrt{\left(4\ln\frac{2}{\pi}\right)}\,\mathrm{S}\ \mathrm{p_{hkl}}\ \mathrm{L(2\theta)F^2(hkl)}\,\exp\left\{\frac{-4\ln 2\,(2\theta_i - 2\theta_{hkl})^2}{H^2}\right\}/H$$

In this case you have used Gaussian function. It could be a combination of Gaussian and Lorentzian function. So, here, you have S, which is Scale factor, it is the same as what we wrote earlier in the first slide. Multiplicity factor (p_{hkl}) Lorentz Factor ($L(2\theta)$), Structure factor($F^2(hkl)$), and this Gaussian function because you have to model the peak and H is the full width half maximum.

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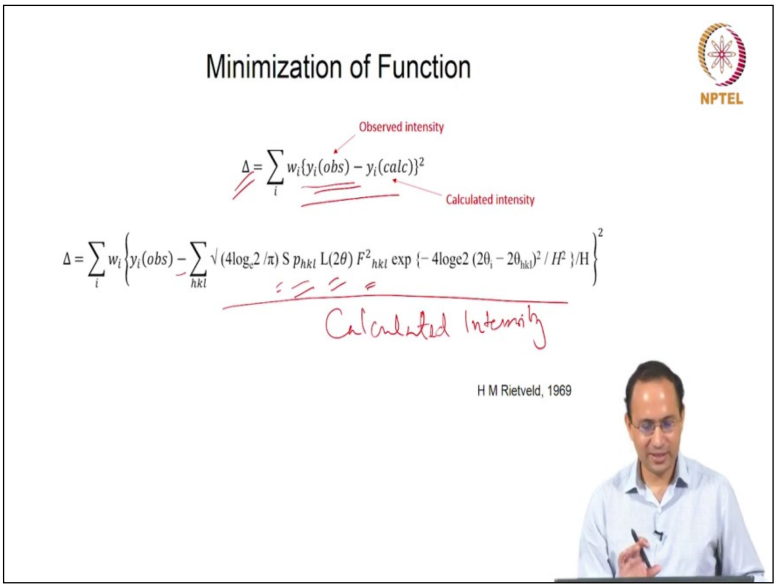

Minimization of Function

Observed intensity

$$\Delta = \sum_i w_i\{y_i(obs) - y_i(calc)\}^2$$

Calculated intensity

$$\Delta = \sum_i w_i\left\{y_i(obs) - \sum_{hkl} \sqrt{}\,(4\log_e 2/\pi)\, S\, p_{hkl}\, L(2\theta)\, F^2{}_{hkl} \exp\{-4\text{loge}2\,(2\theta_i - 2\theta_{hkl})^2/H^2\}/H\right\}^2$$

Calculated Intensity

H M Rietveld, 1969

So, basically what we are doing is we are minimizing Δ.

$$\Delta = \sum_i w_i\{y_i(obs) - y_i(calc)\}^2$$

$$\Delta = \sum_i w_i\left\{y_i(obs) - \sum_{hkl} \sqrt{}(4\ln 2/\pi)\, S\, p_{hkl} L(2\theta) F_{hkl}^2 \exp -4\ln 2(2\theta_i - 2\theta_{hkl})^2/H^2\,/H\right\}^2$$

We are just going over the basic principles. Then we will see one example on how to do it, but this is the principle. So, now all parameters are familiar to you. You know what function to use, if you have asymmetry, how we address it, and all other things we already know.

This multiplicity factor depends on the plane. Lorentz function is dependent on your θ. We discussed about structure factor and you already know how to calculate. Scale factor just takes into account the amount, if you have a mixture, you adjust the scale factor. So, this is like a principle

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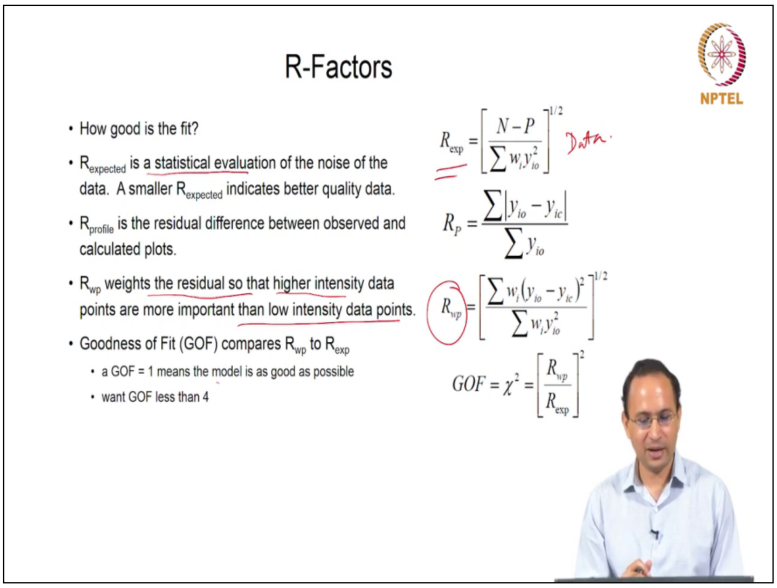

R-Factors

- How good is the fit?
- $R_{expected}$ is a statistical evaluation of the noise of the data. A smaller $R_{expected}$ indicates better quality data.
- $R_{profile}$ is the residual difference between observed and calculated plots.
- R_{wp} weights the residual so that higher intensity data points are more important than low intensity data points.
- Goodness of Fit (GOF) compares R_{wp} to R_{exp}
  - a GOF = 1 means the model is as good as possible
  - want GOF less than 4

$$R_{exp} = \left[\frac{N-P}{\sum w_i y_{io}^2}\right]^{1/2}$$ Data.

$$R_P = \frac{\sum |y_{io} - y_{ic}|}{\sum y_{io}}$$

$$R_{wp} = \left[\frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2}\right]^{1/2}$$

$$GOF = \chi^2 = \left[\frac{R_{wp}}{R_{exp}}\right]^2$$

Then how do we check if you have a good fit or not? That is the question? How do you know whether it is a good fit or not, and so, you do a lot of things. So, when you, you can calculate the $R_{expected}$ these are residuals like $R_{expected}$ can be calculated as this:

$$R_{exp} = \left(\frac{N-P}{\sum w_i y_{io}^2}\right)^{1/2}$$

It tells you about the data quality, what kind of data you have. So, N is your number of data points, P is the profile parameters.

And basically you look at the R_{wp} is the weights of the residual. So, you can see what we are calculating here.

$$R_{wp} = \left(\frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2}\right)^{1/2}$$

And we define Goodness of fit (GOF) as

$$GOF = x^2 = \left[\frac{R_{wp}}{R_{exp}}\right]^2$$

If GOF = 1, means the model is as good as possible, but you never achieve that.

So, we want GOF < 4 which is reasonable.

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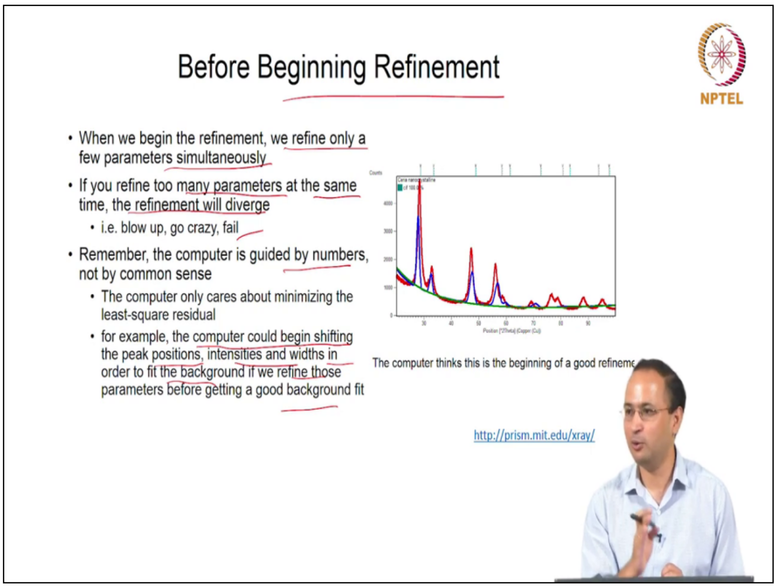

Before Beginning Refinement

- When we begin the refinement, we refine only a few parameters simultaneously
- If you refine too many parameters at the same time, the refinement will diverge
  - i.e. blow up, go crazy, fail
- Remember, the computer is guided by numbers, not by common sense
  - The computer only cares about minimizing the least-square residual
  - for example, the computer could begin shifting the peak positions, intensities and widths in order to fit the background if we refine those parameters before getting a good background fit

The computer thinks this is the beginning of a good refineme

http://prism.mit.edu/xray/

Now, this you can do using software, before you begin refinement, we refine only a few parameters. See, if you refine too many parameters at the same time, the refinement will diverge, it will just blow up. See, in this case, what we see here, the computer could begin shifting the peak positions, intensities and widths, in order to fit the background.

It wants to just minimize the error. So now, if you are shifting the peaks, that is not good, that does not make sense. So there has to be an order as to how you refine. Also, you have to visually observe, basically you are looking at the difference between measured and calculated. So, you have to always look at that, because the computer is guided by numbers, not the common sense, if you tell it to minimize the error it will just do that.

Here you see the peaks are shifted now, in the calculated one, which you do not want. You want a diffraction pattern where you get a peak; the peak has to be, in your calculated pattern also peak should appear there. Otherwise, physically it will not make sense.

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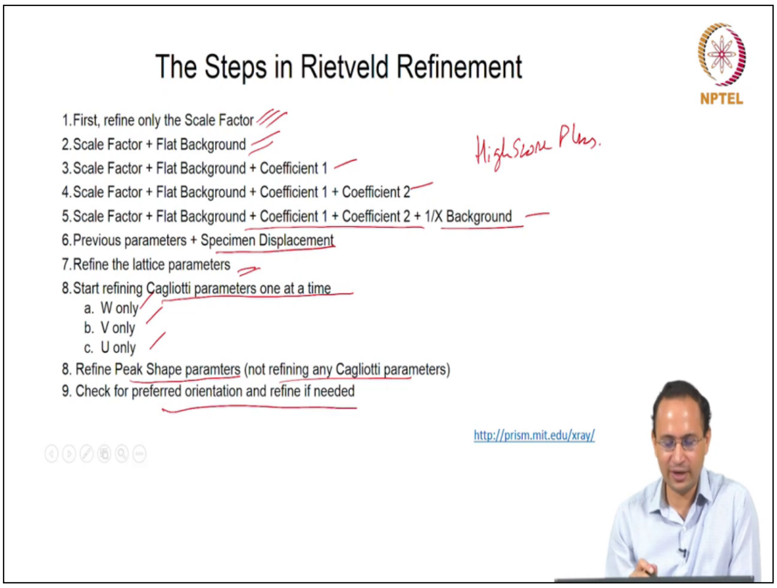

The Steps in Rietveld Refinement

HighScore Plus.

1. First, refine only the Scale Factor
2. Scale Factor + Flat Background
3. Scale Factor + Flat Background + Coefficient 1
4. Scale Factor + Flat Background + Coefficient 1 + Coefficient 2
5. Scale Factor + Flat Background + Coefficient 1 + Coefficient 2 + 1/X Background
6. Previous parameters + Specimen Displacement
7. Refine the lattice parameters
8. Start refining Cagliotti parameters one at a time
    a. W only
    b. V only
    c. U only

8\. Refine Peak Shape paramters (not refining any Cagliotti parameters)

9\. Check for preferred orientation and refine if needed

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So, what are the steps in Rietveld refinement? Now, we know the basics. Basics is that you calculate the intensity. What you have done so far, we have just addressed, we have added a few things like the function, which function to use, which will again depend. Most commonly we use the Pseudo–Voigt function which is the combination of Lorentz and Gaussian functions.

And then, we know this full width half maximum, that varies with your scattering angle, you have to take that into account. So, now we are refining. So, first we have to refine only Scale factor. This is the steps you do in Rietveld Refinement. Unless you do it maybe you will not appreciate, but it's good to follow a guideline. So, first we refine only scale factor.

Then you refine the scale factor and flat background. You are focusing on now the background, which is very important. If you cannot fit it using flat background, you can add coefficients. And you can add $(1/X)$, depends if at lower angles, suppose your background is not flat, there is enough curvature then, you can use these, you can use the background coefficient 1, coefficient 2 and $(1/X)$.

These are the options you have. At least this example is for HighScore Plus. Now you have fit the background. Now, you have to consider the Specimen Displacement, because you have to check whether it is there or not. And then you have to refine the lattice parameters (abc). Then start refining Cagliotti parameters one at a time.

Then, refine the peak shape parameters, are γ, γ_1 γ_2. You have a peak shape, which is combination of Gaussian and Lorentz. So, these are the peak shapes. And then check for preferred orientation and refine it if needed. So one example I will give you.

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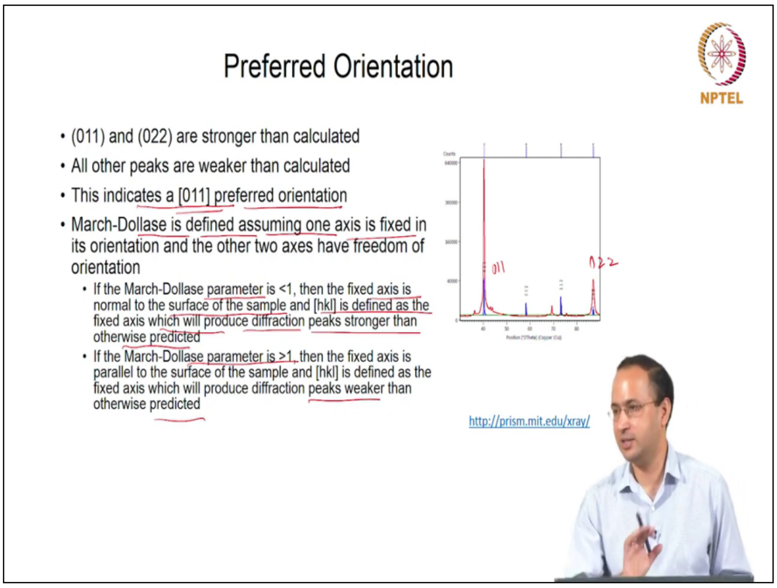

Preferred Orientation

- (011) and (022) are stronger than calculated
- All other peaks are weaker than calculated
- This indicates a [011] preferred orientation
- March-Dollase is defined assuming one axis is fixed in its orientation and the other two axes have freedom of orientation
  - If the March-Dollase parameter is <1, then the fixed axis is normal to the surface of the sample and [hkl] is defined as the fixed axis which will produce diffraction peaks stronger than otherwise predicted
  - If the March-Dollase parameter is >1, then the fixed axis is parallel to the surface of the sample and [hkl] is defined as the fixed axis which will produce diffraction peaks weaker than otherwise predicted

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So in this, what do you see? (In figure in slide) The red one is the calculated one, blue one is measured one. What you see is, the red one intensity is quite high. You see this is (011) plane, this is (022). Why you see both is because, 011, 022 are two parallel planes. But what you see is that the calculated intensity is stronger, that means it tells you, you might have preferred orientation in this case.

So, this indicates [011] plane family has preferred orientation. I mean, this is an extreme example, but I am just showing you. So, how to address that, you can use March-Dollase, you will see that, when you do refinement, we can use this March-Dollase parameter to refine. When you see preferred orientation, then you can use this function.

When the March-Dollase parameter is < 1, then the fixed axis is normal to the surface of sample and [hkl] is defined as the fixed axis which will produce diffraction peaks stronger than otherwise predicted. If the March-Dollase parameter is > 1, then peaks are weaker than otherwise predicted. So, there is a way to address preferred orientation.

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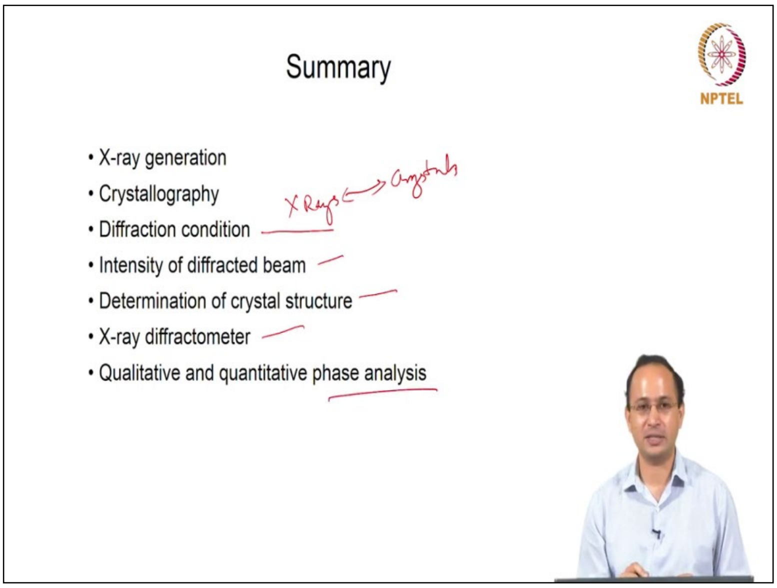

Summary

- X-ray generation
- Crystallography
- Diffraction condition
- Intensity of diffracted beam
- Determination of crystal structure
- X-ray diffractometer
- Qualitative and quantitative phase analysis

So, in the summary what we learnt? We learnt about X-ray generation, crystallography, how these two are connected, how do we use X-rays to probe crystals. then we talked about intensity, how to calculate intensity, how that plays a role. Determination of crystal structure, we saw if you have a diffraction pattern, how you calculate crystal structure, because you have the 2θ intensity values. You get the planes and based on the planes, you see what kind of structure you have. An example, we did.

We looked into X-ray diffractometer and what kind of components it has. Finally we looked into qualitative and quantitative phase analysis. So this completes our basics on X-ray diffraction.

In the next class, we will learn about the sample preparation for cementitious materials and application of XRD in cementitious materials. Now you have enough background, you know what is X-ray diffraction, how do we apply to cement-based materials, that will be discussed in next lecture.